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Phosphorus forms of the surface sediment in the Iranian coast of the Southern Caspian Sea

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ABSTRACT
Sediments from the Southern Caspian Sea, located in Iranian coast were examined on the basis of P-fractionation (five forms of phosphorus) by a sequential extraction scheme. Ninety-six surface sediment samples (for each season with triplicate) were collected from eight sampling transects in 10 and 100 m depths during summer and winter in 2010-2011. The result indicated that the most abundant forms of phosphorus were calcium bound phosphorus. Relative abundance of other forms of phosphorus follow the order: organic-P>Fe-P>Al-P>Absorbed-P. The loosely absorbed phosphorus represented <1% of the sedimentary inorganic phosphorus, while the Fe/Al phosphorus ranged 5–6%.The calcium bound phosphorus showed considerable contribution (88%) to the sedimentary inorganic P-loads.

Key words: Caspian coastline, Rice, Pesticides, Mineral elements

INTRODUCTION

Phosphorus (P) is one of the vital elements for life on earth and plays an important role in the biological productivity in oceans. The sorption of phosphorus on sediments has a major influence on transport, degradation, and ultimate fate of phosphorus in marine ecosystems. On the other hand, impact of sedimentary phosphorus in aquatic ecosystems depends on its chemical composition and form in the sediment. For this reason, various forms of phosphorus in the sediment are considered (Huang *et al.*, 2005). Phosphorus is generally regarded as one of the key factors for the eutrophication (Khalil & Rifaat, 2013). As an internal source, phosphorus released from the sediment (Zhou *et al.*, 2001;Hanrahan *et al.*, 2005) may contribute at an important level compared with external sources such as atmosphere deposits, agricultural runoff and wastewater discharges (Wang *et al.*, 2006; Wang *et al.*, 2007). However, not all of phosphorus forms are likely to be released from the sediment and thereby render lake eutrophic (Aviles *et al.*, 2006). Phosphorus fractionation is a key to understanding phosphorus mobility in the lake sediments (Aviles & Niell, 2005). Many chemical sequential extraction procedures (Das *et al.*, 2001; Cha *et al.*, 2005; Porrello *et al.*, 2005; Ruiz-Calero & Galceran, 2005) have been applied to assess the mobility and bioavailability of phosphorus in lake sediments (Worsfold *et al.*, 2005;Apostolaki *et al.*, 2007). Pervious study conducted on the distribution of phosphorus (total P, organic and inorganic P) in the Southern of Caspian Sea sediments in the summer 2009 using different methods which revealed that the most abundant forms of phosphorus was authigenic phosphorus (Samadi-Maybodi *et al.*, 2013). The purpose of this study was to investigate the different P-forms present on the surface sediment of Southern Caspian Sea-Iranian coast. Labile, loosely bound or exchangeable P fraction; Fe/Al-P fraction is usually associated with Al, Fe and Mn oxides and hydroxides; Ca-P fraction is formed from the adsorption of P on calcium carbonate and precipitation of calcium phosphates; organic P fraction is more complex and less understood.

MATERIALS AND METHODS

STUDY AREA

The Iran's coastline is about 900 kms long. The area includes 3 regions from east to west namely; Golestan, Mazandaran and Guilan with a combined population of about 6.4 million which is 10% of the total population of the country (CSN, 2003). The bottom sediments of the Caspian Sea are represented by calcareous and terrigenous deposits. In the North Caspian, coarse-grained sediments such as silts and terrigenous sands dominate. On the western shelf and slope of the Middle Caspian, down to sea depths of 30–60 m, terrigenous silts prevail. In the western shelf of the South Caspian, a gradual replacement of sands-grained by weakly calcareous silts and the floor of the deep-water part of the South Caspian basin is covered with weakly calcareous clayey silts. The calcareous clayey silts also cover on the eastern part of the South Caspian (Kosarev, 2005).

SEDIMENT SAMPLING AND ANANLYSIS

Surface sediment samples were collected within the framework of the "Hydrology and Hydrobiology study of the Southern Caspian Sea-Iranian coast" project which was carried out in 2010-2011. Ninety-six (with triplicate) samples were collected using Van Veen Grab Sampler from the eight transects (1=Astara, 2=Anzali, 3=Sefidrod, 4=Tonekabon, 5=Noshahr, 6=Babolsar, 7=Amirabad and 8=Turkman) in the Iranian coast of the Southern Caspian Sea (Fig.1). The 0–5 cm layer was sampled. Two cruises were carried out on board the R/V Guilan during the two seasons (once in summer and once in winter). Two sampling periods were chosen in summer (warm and algal bloom seasons) and winter (cold season) for comparison purposes. Along each transect, two stations were located at water depths of 10 and 100 m. The selected sampling stations were located inshore (10 m depth) and offshore (100 m depth) zone for comparison purposes. The sediment samples were taken to the laboratory in sealed plastic bags that were put in iceboxes (<4ºC). The samples were freeze-dried before analysis. They were then homogenized for experiments. In addition, overlying water samples were collected with a one liter Ruttner sampler in the 10 and 100 m depths. The samples were kept in 1-litre polyethylene bottles and placed on ice. In the laboratory the samples were kept in the dark and frozen (-20 °C) until they were analyzed. The analysis of overlaying water was made by molybdenum blue/ascorbic acid method (APHA, 2005).

PHOSPHORUS FRACTIONATION

The phosphorus fractionation method used in the present work was the (Psenner & Pucska, 1988) scheme and modified by HUPFER (Aviles *et al.,* 2006). This extraction method draws the conclusion on the P-binding forms in the sediments (Table 1), and is also useful to predict bioavailability of P. After each extraction step, samples were extracted at room temperature in an overhead shaker and the supernatant was filtrated through a 0.45 µm membrane. The analysis of DRP (Inorganic-P) was made by using molybdenum blue/ascorbic acid method (APHA, 2005).

Total P (TP=DRP+NRP) was measured by applying Valderrama (1981) method treated by persulfate reagent and further analyzed as a DRP sample. The NRP (Organic-P) fraction is defined as the difference between TP and DRP. With this extraction procedure, as shown in Table 1, phosphorus is fractionated in labile P ($NH4Cl$= Absorbed-P), redox-sensitive P (bicarbonate-dithionite = Fe-P), metal oxide bound P (NaOH-P = Al-P), Ca bound P (HCl-P = Ca-P). Bioavailable-P is the sum of dissolved reactive phosphorus (DRP) in the three fractions (Absorbed-P, Fe-P and Al-P).

All samples at each fraction were analyzed in triplicate and the data were expressed as mean and standard error. Total organic matter (TOM) in sediments was analyzed as the loss of ignition at 500 ºC for 2 h (Jensen & Anderson, 1992).

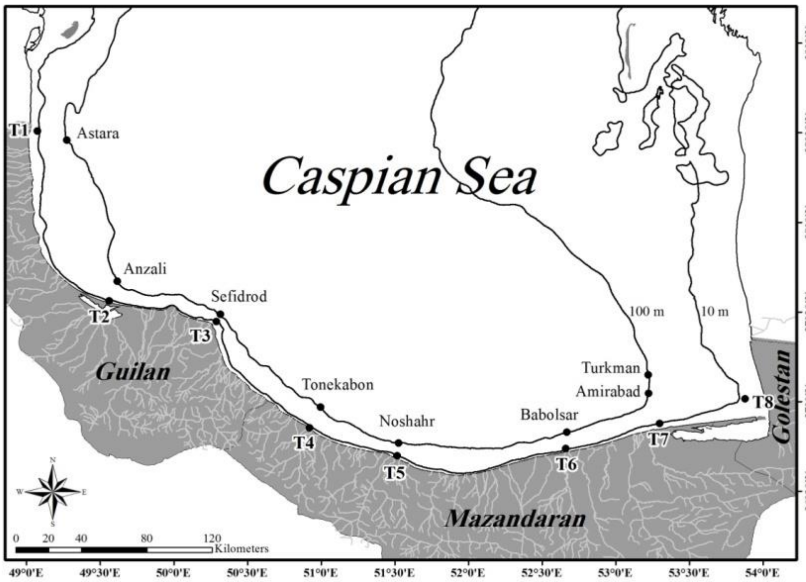

Fig.1. Map of the Caspian Sea showing the sampling stations in the southern Caspian Sea-Iranian coast

Table 1. Extraction procedure used in the present work, adapted from (Psenner and Pucsko, 1988) extraction scheme (DRP–Dissolved Reactive Phosphorus; NRP–Non Reactive Phosphorus; TP–Total Phosphorus)

Step	Solvent	P-fractions	P-bounding form
1	NH4Cl (Absorbed-P)	DRP	Loosely bound P: Pore water soluble phosphate and sediment surface loosely adsorbed phosphate, algal available phosphate
		NRP	
2	BD (0.11 M) (Bicarbonate Dithionite) (Fe-P)	DRP	Reductant soluble P: Redox-sensitive P, mainly bound to Fe-hydroxide and Mn-hydroxide
		NRP	Redox-sensitive organic P
3	NaOH (1 M) (Sodium Hydroxide) (Al-P)	DRP	Metallic oxide bound P: Phosphate bound to metallic oxide (mainly Al), soluble inorganic P compounds in alkaline solution
		NRP	P in micro-organisms, detritus, humic compounds, poly-P, P-lipid
4	HCl (0.5 M) (Ca-P)	DRP	(Hydrochloric acid) SRP Apatite and CaCO3 bound P Organic P sensible to acid
		NRP	

DATA TREATMENT AND TESTING FOR APPROPRIATENESS

Employing the Shapiro-Wilk test, the result revealed that the data transferred was normal. Also, by using the Box's test, we showed that the datasets fit the third requirement, i.e. homogeneity of variance. Finally, all cases with outliers using box plot graph were eliminated. To examine the validity and suitability of these data for the PCA, two widely used statistical tests, namely Kaiser–Meyer–Olkin (KMO) test which measures sampling adequacy and Bartlett's tests, were performed (Ghiyasv, 2008). In this study, KMO coefficient was equal to 0.51. Bartlett's test is used to test the null hypothesis that the variables are uncorrelated in the population (Hair *et al.,* 1998) which was significant ($p<0.01$).

All data obtained from the two sampling periods were used for statistical analyses, which were achieved by using SPSS 11.0 software.

RESULTS

OVERLAYING WATER

In the overlying waters, DO% ranged from 62% to 160% in summer and from 87% to 146% in winter. Accordingly, the oxic conditions could be dominant at the sampling sites during summer and winter. The pH was observed more than 8.00 during two seasons. The mean of the temperature was obtained at less than 11.00 during summer and winter at 10 and 100 m (except at 10 m in summer). Three forms of P at overlying water of 10 m depth was more than 100 m depth during both seasons (Table 2).

SURFACE SEDIMENTS

As shown in Table 3, the concentrations of total phosphorus (Fe-TP, Al-TP and Absorbed-TP) in the sediments in the 100 m were higher than those in the 10 m depth, while for Ca-TP in the 10 m were higher than those in the 100 m depth. However, the concentrations of Fe-TP, Al-TP in the sediments in the 100 m depth were significantly different with the 10 m depth sediments ($p<0.05$). In addition, the concentrations of TP (except Fe-TP) in most sediment showed a little variation between summer and winter ($p>0.05$). The concentrations of inorganic P (DRP) and organic P (NRP) of Absorbed form were higher in the 100 m than in the 10 m depth, but showed a little variation between these two depth and seasons. Fe/Al-P concentrations were less than 100 µg/g Fe/Al-P (Table 3). The spatial variation of Ca-P concentrations (DRP and NRP forms) showed a similar trend, but was not as obvious as that of Absorbed-P concentrations from summer to winter. The concentrations of Bioavailable-P (Fe/Al-DRP and Absorbed-DRP) in the sediments had increased from summer to winter, especially in Fe-DRP (increasing about 10%).

However, NRP concentrations tended to decrease with small variations. Ca-P (DRP and NRP) tended to decline from summer to winter (decreasing from 7% to 13%).

Results of current study indicated that the most abundant forms of phosphorus were Ca-DRP. Relative abundances of other forms come the following order: Fe-DRP>Al-DRP>Absorbed-DRP. The

Absorbed–DRP represented<1% of the sedimentary inorganic phosphorus, while the Fe–DRP and Al-DRP ranged 5–6%. The Ca–DRP showed considerable contribution of 88%. The most abundant organic forms of phosphorus was Ca-NRP.

Relative abundances of other forms of (NRP) follow the order: Al-NRP>Fe-NRP=absorbed-NRP. The absorbed –NRP and Al-NRP represented 5% of the sedimentary organic phosphorus, while the Fe–NRP was 12%. The Ca–NRP showed considerable contribution of 78%. The mean of Bioavailable-P (122 ± 8 $\mu g.g.dw^{-1}$) was more than organic-P (NRP) (59 ± 4 $\mu g.g.dw^{-1}$) during two seasons. The percentage of Bioavailable-P was less than 20% and for phosphorus bounded with Ca-DRP was more than 80% at different depths and seasons (Fig. 2). Overlying-water DIP concentration varied between 0.15 and 0.63 µM, with the highest concentration at 10 m depth (Anzali transect) in winter (Fig. 3). Bioavailable-P concentrations in the surface sediments were always higher than these values (DIP). Nonetheless, the concentration of Bioavailable-P ranged between 66 and 209 $\mu g.g.dw^{-1}$ in the surface sediment on all sampling data.

The TOM% varied between 0.72 and 7.31 in the sampling area. The mean of TOM% (±SE) was observed at 3.76±0.54 and 3.55 ± 0.45 in summer and winter, respectively. In addition, the mean of TOM% (± SE) was registered at 2.29 ± 0.38 and 4.94 ± 0.32 in the 10 m and100 m depths, respectively. However, the TOM% in the sediments in the 100 m depth was significantly different with the 10 m depth sediments ($p<0.05$), while, the TOM% indicated a little variation between summer and winter ($p>0.05$).

PCA was applied to the 9 variables collected during the two seasons (Table 4). The results of PCA test disclosed that three main factors were enough to explain more than 76.2% of cumulated variance. PC1 and PC2 account for 34.1% and 24.8% of the total variance, respectively. PC1 explained TOM% and total phosphorus and inorganic phosphorus compound which are bounded with Fe and absorbed factors, while PC2 included Ca-TP, Ca-DRP and Absorbed-DRP.

PC3 explained relatively lower variance (20.0%) with a high loading factor on total and inorganic phosphorus compound bounded with Al.

Table 2. Mean (±SE) of some physico-chemical characteristics of overlay water body during different seasons and depths in the southern Caspian Sea (2010-2011).

	Summer		**Winter**	
	10 m	100 m	10 m	100 m
pH	8.38 ± 0.04	8.32 ± 0.06	8.35 ± 0.05	8.39 ± 0.05
DO%	130 ± 6	74 ± 5	134 ± 4	91 ± 3
Temperature (ºC)	30.29 ± 0.45	8.36 ± 0.25	9.29 ± 0.63	10.39 ± 0.21
DIP (µM)	0.29 ± 0.04	0.32 ± 0.03	0.33 ± 0.06	0.25 ± 0.03
DOP (µM)	0.60 ± 0.11	0.50 ± 0.08	0.60 ± 0.13	0.52 ± 0.11
TP (µM)	0.89 ± 0.15	0.82 ± 0.08	0.92 ± 0.13	0.77 ± 0.09

Table 3. Mean (±SE) of different forms of phosphorus during different seasons and depths in the southern Caspian Sea surface sediments (2010-2011).

			Summer 2010		**Winter 2011**	
			10 m	100 m	10 m	100 m
Absorbed-P	TP	Mean ± SE	22.88 ± 1.87	23.35 ± 0.88	20.97 ± 2.08	22.06 ± 2.67
	DRP	Mean ± SE	7.45 ± 0.80	9.77 ± 1.07	8.78 ± 1.16	10.19 ± 1.28
	NRP	Mean ± SE	15.41 ± 1.76	13.59 ± 1.23	13.09 ± 2.31	13.38 ± 2.22
Fe-P	TP	Mean ± SE	60.75 ± 4.00	66.08 ± 5.78	59.44 ± 6.27	89.05 ± 8.64
	DRP	Mean ± SE	45.18 ± 5.01	57.52 ± 5.68	53.87 ± 3.46	84.04 ± 3.18
	NRP	Mean ± SE	15.68 ± 3.69	9.68 ± 4.25	13.28 ± 3.23	16.61 ± 4.15
Al-P	TP	Mean ± SE	65.79 ± 6.30	73.79 ± 5.54	66.96 ± 11.26	109.22 ± 5.12
	DRP	Mean ± SE	48.27 ± 2.93	27.21 ± 4.74	43.45 ± 7.56	71.61 ± 5.72
	NRP	Mean ± SE	19.29 ± 4.71	46.06 ± 2.66	23.67 ± 5.18	39.50 ± 5.21
Ca-P	TP	Mean ± SE	1431.86 ± 111.02	1121.16 ± 49.74	1039.62 ± 69.32	921.01 ± 33.71
	DRP	Mean ± SE	1146.18 ± 114.95	917.33 ± 69.18	770.43 ± 88.83	819.63 ± 20.51
	NRP	Mean ± SE	238.01 ± 58.02	210.17 ± 39.00	305.90 ± 59.93	107.93 ± 28.31

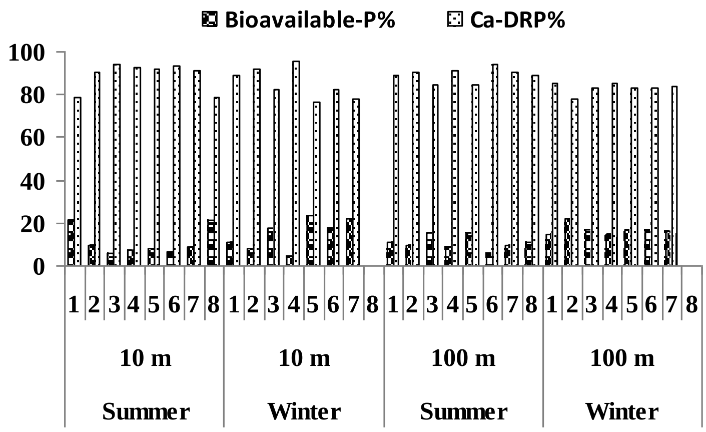

Fig. 2. Percentage of Bioavailable-P and Ca-DRP at different depths and seasons in the southern Caspian Sea surface sediment (2010-2011).

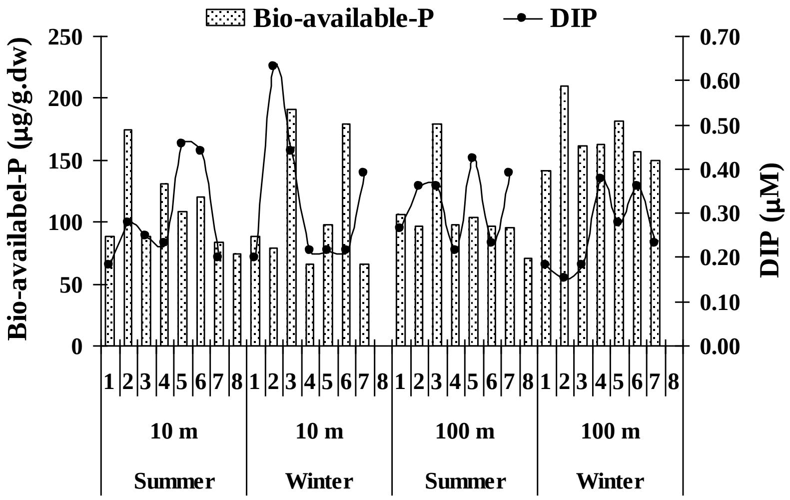

Fig. 3. Concentrations of Bioavailable-P at surface sediments and DIP of overlying water body at different depths and seasons in the southern Caspian Sea (2010-2011).

Table 4. PCA results from correlation matrix at the different depths in the Southern Caspian Sea surface sediment of the Iranian coast.

	Component		
	PC1 (31.4%)	**PC2 (24.8%)**	**PC3 (20.0%)**
Absorbed-TP	0.543		
Absorbed-DRP	0.491	-0.635	
Fe-TP	0.902		
Fe-DRP	0.926		
Al-TP			0.918
Al-DRP			0.940
Ca-TP		0.929	
Ca-DRP		0.930	
TOM%	0.732		

Extraction Method: Principal Component Analysis.
Rotation Method: Varimax with Kaiser Normalization.

DISCUSSION

Results of the current study indicated that the most abundant forms of phosphorus was Ca-P. Relative abundances of other forms of phosphorus follow the succeeding order: organic-P>Fe-P>Al-P>Absorbed-P. The loosely absorbed phosphorus (NH_4Cl–P) represented <1% of the sedimentary inorganic phosphorus, while the Fe/Al phosphorus (BD–P, NaOH-P) ranged 5–6%.The calcium bound phosphorus (HCl–P) showed considerable contribution (88%) to the sedimentary inorganic P-loads. Therefore, retention of P the sediments is governed largely by the presence of Ca bounded species in the Southern Caspian Sea. Samadi-Maybodi *et al.* (2013) noted the most abundant forms of phosphorus was authigenic species at the Southern Caspian in summer 2009 which was confirmed by the current study. The BD-P represents the redox-sensitive P fraction, mainly including P bound to Fe-hydroxides and Mn compounds (Kleeberg & Gruenberg, 2005), which are considered as potentially mobile pool of P (Rydin, 2000). Meanwhile, PCA analysis showed that Fe-DRP was the most important variable with high loading factor at PC1 which had probably a principal role to release phosphorus into the water column. Further, NaOH-P which refer to P bound to metal (hydr) oxides, mainly of Al, and is exchangeable with OH-, was used to estimate available P in the sediment, and as an indicator of algal available P (Zhou *et al.,* 2001). In the current study, although Al=DRP was associated with PC_3 even though it contained high loading factor, the variance and concentration could play principal role in releasing into the overlaying water. The bio-available phosphorus that mainly includes NH_4Cl-P, BD-P and NaOH-P indicated that the rank order of the P-fractions in the study site was NaOH-P>BD-P>NH_4Cl-P, and the total phosphorus of the sediment were dominated by bio-available P (the proportion is up to 53%). Potentially the bio-available phosphorus can contribute substantially to the local primary production when the fraction reaches the water column during its growing season. As a result, the sediments in the study site are at high risk to release phosphorus under certain environmental conditions. Nowadays, many bodies of water in the world (e.g. The Caspian Sea) are mezo-eutrophic and experiencing an increased number of harmful cyanobacteria blooms (Hart *et al.,* 2003; Kong & Gao 2005; Soloniev, 2005; Nasrollahzadeh, 2008; Nasrollahzadeh *et al.,* 2008; Nasrollahzadeh *et al.*, 2011). Nasrollahzadeh *et al*. (2012) also reported that Caspian ecosystem was limited in nitrogen the before introduction of *Mnemeiopsis leidyi*, while it seems that after the introduction of *M. leidyi* the system has been shifted to phosphorous limitation. Hence, sediment phosphorus has probably been recognized as the most critical nutrient for algal bloom events. The concentration of phosphorus in the sediment is often 1000-fold higher than that in the water column. Therefore, bio-available P in the sediment can be released under a range of biogeochemical conditions, which is mainly controlled by redox status and pH values that induce phosphorus release from the inorganic P pool by desorption processes or from the organic pool by mineralization (Jensen & Andersen, 1992; Gardolinskia *et al*., 2004; Zhou *et al.,* 2005). In the current study, the results revealed that the concentration of bio-available P in the sediment is often 10000-fold higher than that in overlaying water layer, which is an indication that this is even more than the other lakes. In addition, the percentage of bio-available P (out of DRP) was obtained 8.1% to 16.8% in 10 and 100 m depths during summer and winter, respectively. Zhou *et al.* (2001, 2005) noted that under severe conditions of high pH, anaerobic conditions and disturbance not only was the P concentration of the overlying water that decreased immediately to a very low level, but also the proportion of bio-available phosphorus in the sediment was reduced and a majority of which were replaced by non-reactive species. In the current study, the pH of water were high (>8.00). Anaerobic conditions and disturbance by fish and any physical condition could cause the bio-available phosphorus release into the water column the result of which was similar to the aforementioned research. Lots of factors can affect the release of phosphorus from sediment. Besides the physical and chemical components of sediment itself, disturbance, high temperature (>15°C), high pH（pH>8.0, low P concentration of the overlying water and anaerobic conditions may favour phosphorus release from the sediment. Huang *et al*. (2005) noted that higher pH weakened the association of phosphates with the Fe/Al hydroxides and then resulted in Fe/Al-P release. The increase of pH was accompanied with autogenetic progresses of calcium carbonate and the elevated Ca-P concentrations in the sediments. In the Caspian Sea surface sediments, result indicated that aerobic (under saturation) conditions could not stimulate P release. Moreover, only Fe-DRP negatively correlated with DO% values in the overlying waters (regression coefficient=-0.493) and release from sediments at location with low DO%. Meanwhile, pH value was another important factor affecting the release of phosphorus from sediments, especially under alkaline condition, which promoted the NaOH-P release greatly (Jin *et al.* 2004). In fact, pH values were high in the overlying water that promoted the NaOH-P release because ligand competition between $PO4^{-3}$ and OH^- in the sediments would cause the availability of binding sites on ferric complexes to decrease (Andersen, 1975; Lijklema, 1980) so the concentrations and percentages of Fe/Al-P in the sediments would also decrease into the water column. In the current study, the pH of overlying water were high (>8.00) but no correlation between bioavailable-P and pH was observed. This is an indication that high pH could cause release of bioavailable-P continuously from sediments into the overlying water when other conditions were suitable. Under the condition where both high pH value and aerobic are high, a great deal of phosphorus released from sediment, disclose that aeration couldn't restrain P release under high pH condition, not to mention the high pH coupled with anaerobic condition. When TP concentration in the overlying water was high, phosphorus in water column would not be absorbed by sediment under anaerobic conditions. Temperature was one of the parameters for controlling the release of phosphorus from sediment. In the Caspian Sea, result of overlying water column indicated that in summer temperature of 10 m depth promoted P release greatly, but other depth and seasons could not affect releasing different forms of P because of low temperature (Table 2). In addition, the result also showed that only Al-DRP positively correlated with temperature values in the overlying water (regression coefficient = 0.440) and probably release from sediments at location with high temperature especially in summer at 10 meter depth.

CONCLUSION

Sediment processes regulating available P may be important regulators of internal P recycling and consequently lake trophic status. Our data suggest that under Caspian conditions sediment available P will be released to the water column which could confirm the recently Cyanophyta bloom events in the Caspian ecosystem. In addition, total organic matter of sediment was increased because of *M. leidyi* existence. Therefore, this phenomenon confirms higher concentration of Ca-P than other P forms.

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اشکال مختلف فسفر در رسوبات سطحی سواحل حوزه جنوبی دریای خزر- سواحل ایران

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چکیده

در این تحقیق پنج شکل فسفر در رسوبات سطحی حوضه جنوبی دریای خزر- سواحل ایران بر اساس استخراج متوالی اندازه گیری شد. تعداد ۹۶ نمونه از رسوبات سطحی (برای هر فصل با سه تکرار) در هشت نیم خط و در اعماق ۱۰ و ۱۰۰ متر طی فصول تابستان و بهار سال ۱۳۹۱ جمع آوری شد. نتایج این تحقیق نشان داد که فراوان ترین شکل از میان پنج شکل استخراج شده متعلق به فسفر متصل به عنصر کلسیم بوده است. فراوانی نسبی چهار شکل دیگر فسفر از زیاد به کم به صورت فسفر آلی> فسفر متصل به آهن> فسفر متصل به آلومینیم> فسفر متصل سطحی ثبت شد، به طوری که درصد غلظتی فسفر متصل سطحی برابر کمتر از ۱٪ و مجموع فسفر متصل به آهن و آلومینیم برابر ۵٪ تا ۶٪ درصد بوده است. همچنین فسفر متصل به کلسیم دارای درصد غلظتی ۸۸٪ بوده است.

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